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Optical Properties of a [111] UO₂ Crystal and U₃O₇ Formation at Room Temperature Investigated by Raman, Ellipsometric and Transmission Spectroscopy.

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October 22, 2009

CASS

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Optical Properties of an [111] UO_2 Crystal
and U_3O_7 Formation at Room Temperature
Investigated by Raman,
Ellipsometric and Transmission Spectroscopy.

28th

Compatibility, Aging & Stockpile Stewardship Conference
September 29 – October 2, 2009
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Lawrence Livermore National Laboratory

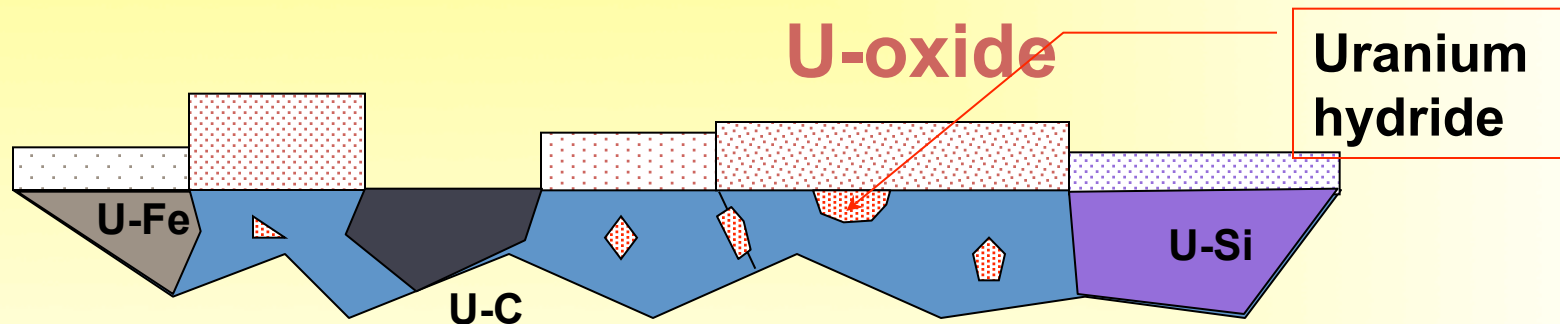
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*Reviewed by
Bart Ebbinghaus
9/25/09*

Motivation: The Uranium oxide layer controls U-hydriding. We need non-destructive tools to understand and measure it.

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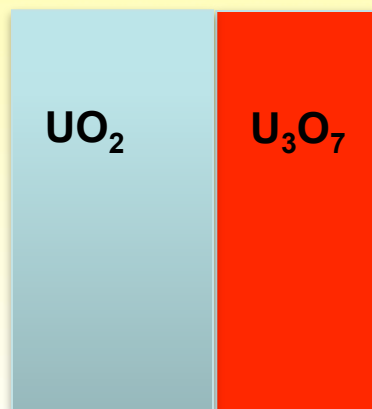
- The **local** properties of the oxide layer on uranium
 - its **moiety**, its thickness, its impurity content, its integrity
 - control the **local** initiation time of Uranium hydriding,
 - *at the site with the lowest hydrogen diffusion impedance*
- *Uranium has many impurities and oxidation states*



- Optical techniques have high ($< 10\mu\text{m}$) spatial resolution
- To make use of them it is essential to know the optical constants of the different uranium oxidation states (moieties)

Summary: We analyze UO_2 by ellipsometry and Raman spectroscopy and conclude that the literature values of 1) the optical constants of UO_2 and 2) the low temperature oxidation rate of UO_2 are probably incorrect.

- **1)** UO_2 is the simplest oxide moiety. We measured the optical constants $\varepsilon_1, \varepsilon_2$ of the [111] surface of a single crystal of UO_2 using ellipsometry. Our values *disagree* with the only literature values, Schoenes (J.Appl.Phys.**49**,1978)
 - Schoenes used near normal incidence reflectivity between .03 and 13eV of vacuum annealed [111] UO_2 to *derive* its dielectric constants $\varepsilon_1, \varepsilon_2$ by means of the Kramers-Kronig relation
 - We used Raman spectroscopy at normal and off-normal (75°) incidence to prove our sample to be UO_2



- **2)** We examined the oxidation of a UO_2 (111) surface after exposure to air for ~ 25 years at room temperature. Literature¹ predicts a 8nm thick U_3O_7 layer. Our data disagree: Raman spectra acquired at 633 nm and at angles of incidence of 0° and 75° are consistent with pure UO_2

¹Poulesquen, A., L. Desgranges, et al. (2007). J. Nuclear Materials 362(2-3): 402-410.

Our sample: a small piece of single crystal UO_2 [111], mechanically polished at LANL*, exposed to air since ~ 1984

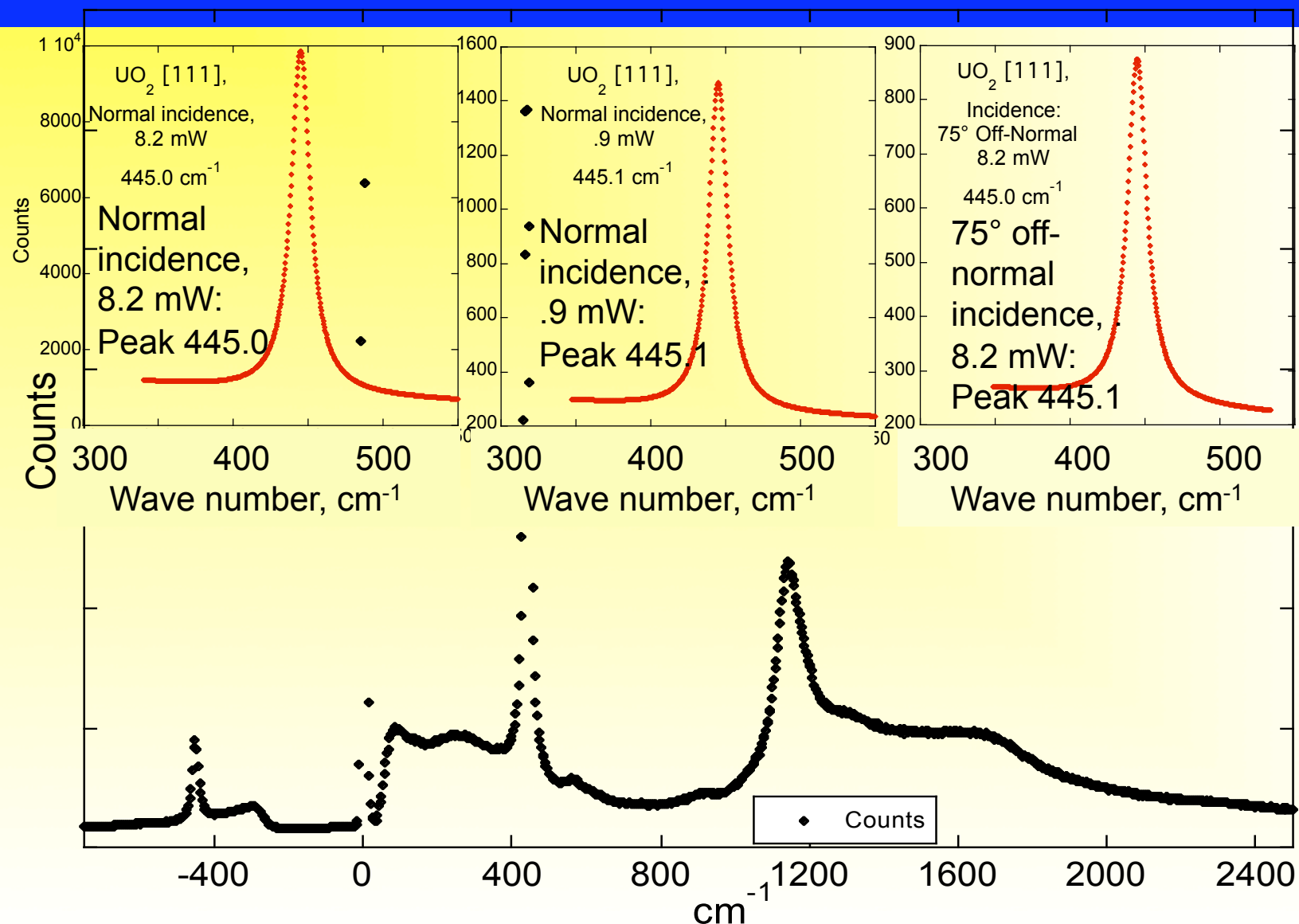
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500.0 μm

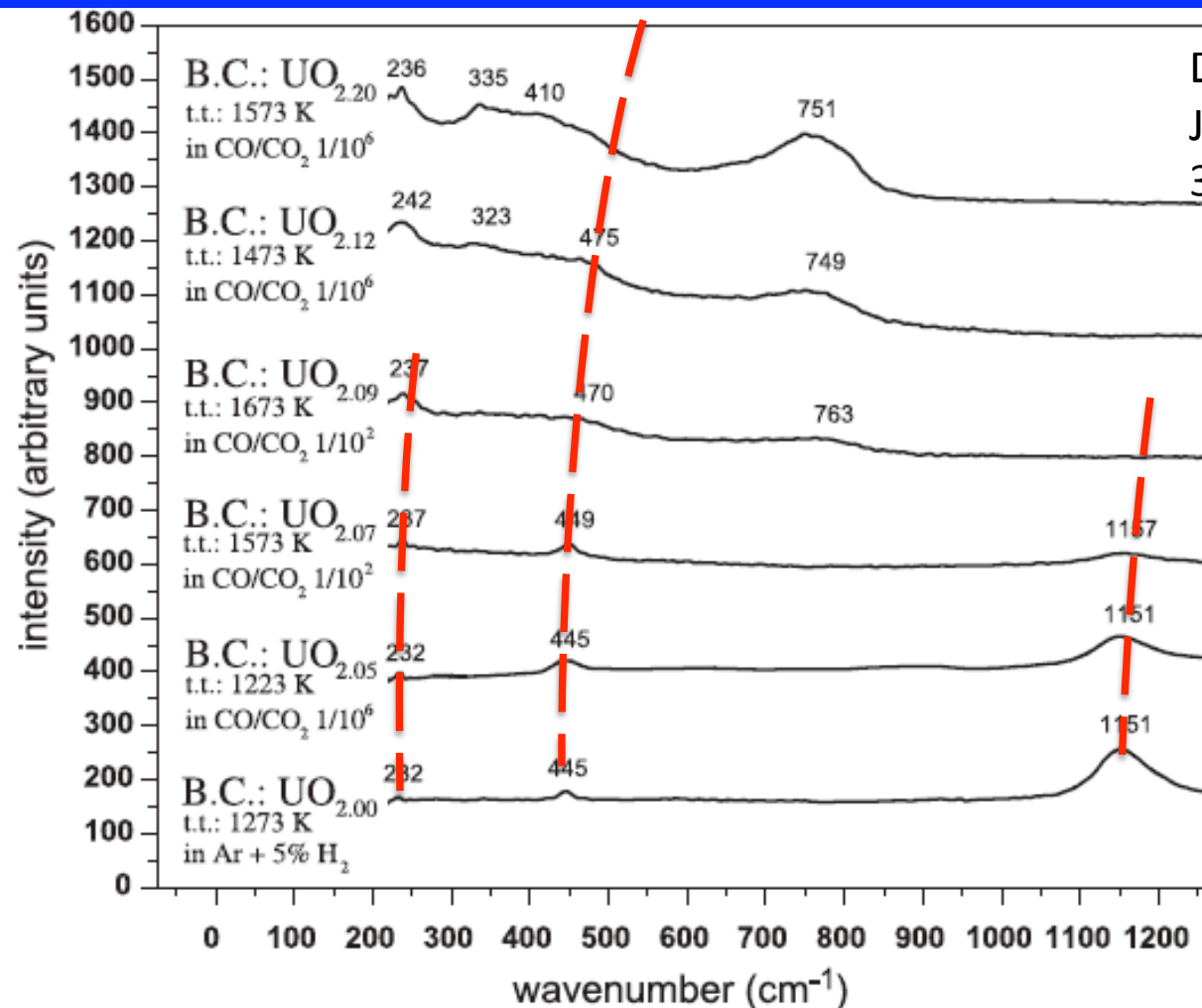
100.0 μm

- * Courtesy of Dr. R. Schulze, LANL

The sample is pure [111] UO_2 : it shows at low and high power only UO_{2+0} Raman lines (632 nm laser) at low and high resolution, even at 75° off-normal laser incidence, where 28% of the signal originates from 7 nm near the surface.



Our [111] UO_2 sample shows none of the Raman lines characteristic of hyper-stoichiometric Uranium oxide, it is consistent only with $\text{UO}_{2+\delta}$



D. Manara, B. Renker
J. Of Nucl. Materials
321(2003) 233-237

In contrast: Our Raman spectra do NOT show any shift at 232, 445, nor near 1150 cm^{-1} , NEITHER the appearance of a peak near 750 cm^{-1}

Fig. 1. Raman spectra measured on oxidised UO_{2+x} samples of several oxidation levels. Beside each spectrum are indicated the bulk composition (BC) of the corresponding specimen and the thermal treatment (tt) to which the specimen was subjected. The bulk composition corresponds to the composition of the surface in slightly oxidised samples ($\text{O}/\text{U} \leq 2.07$). The superficial composition of more oxidised samples is unknown, due to the precipitation of higher oxides on the surface in contact with air.

Our [111] UO_2 sample shows –even at 75° off-normal incidence- none of the Raman lines characteristic of “oxidized” UO_2 , as defined by Allen et al.

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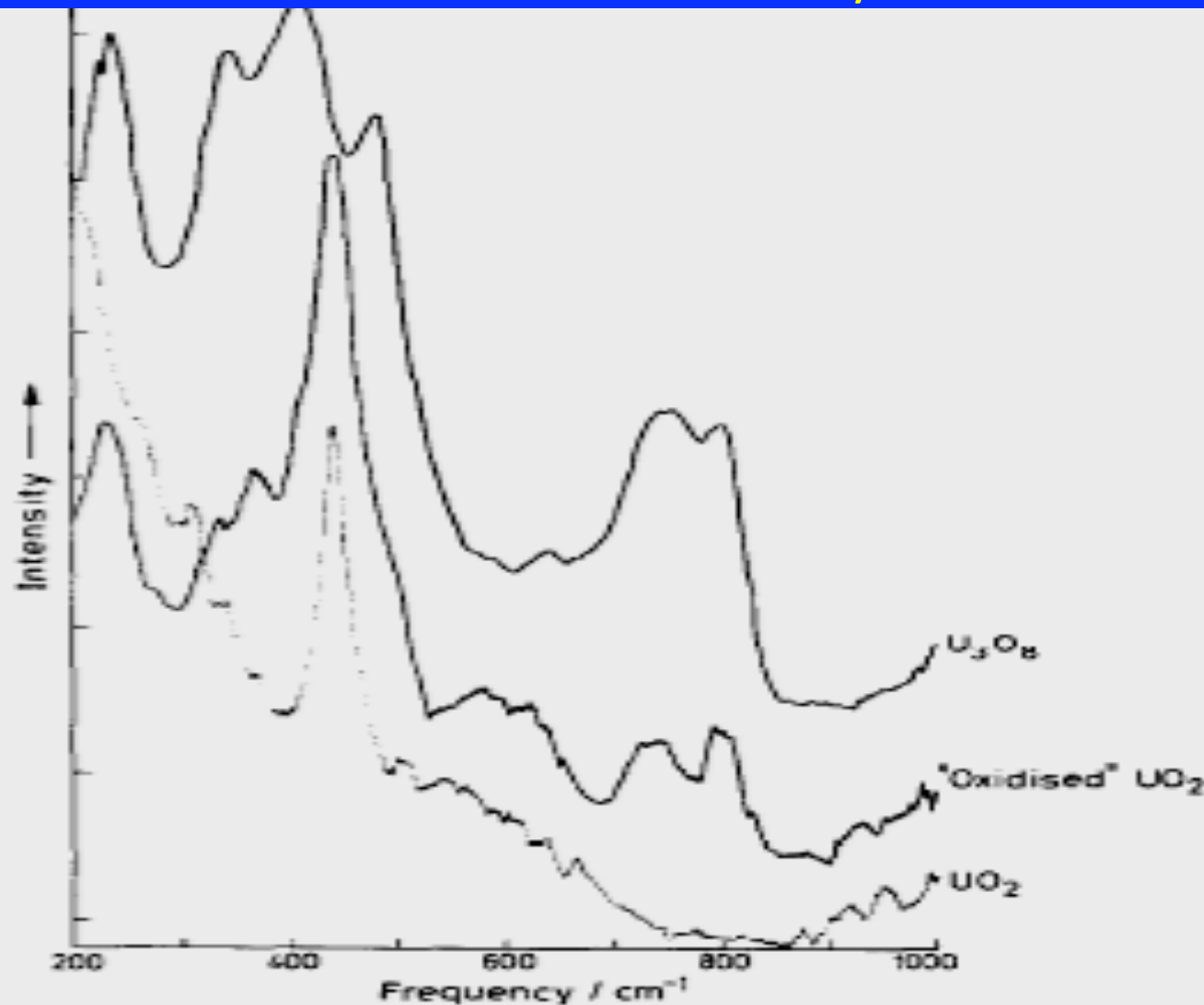
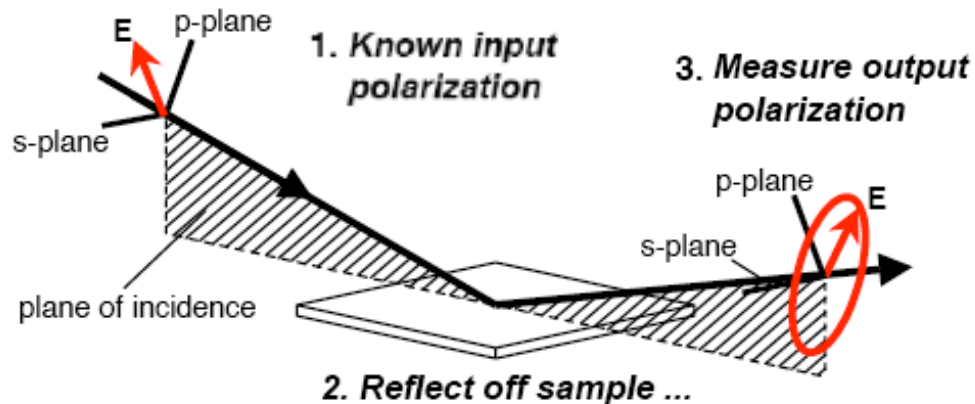


Fig. 2. Raman spectra of UO_2 , UO_2 oxidised in laser beam, and U_3O_8 .

Allen, G. C., Butler,
I.S., Anh Tuan, N.
J. Of Nuclear
Materials
144 (1987) 17-19

We use ellipsometric spectroscopy (a very robust technique compared to Schoene's reflectometry) to get UO_2 's complex reflection coefficient ρ as $f(\text{photon energy})$ and $(n, k, \epsilon_1, \epsilon_2)$ by fitting optical models to data.

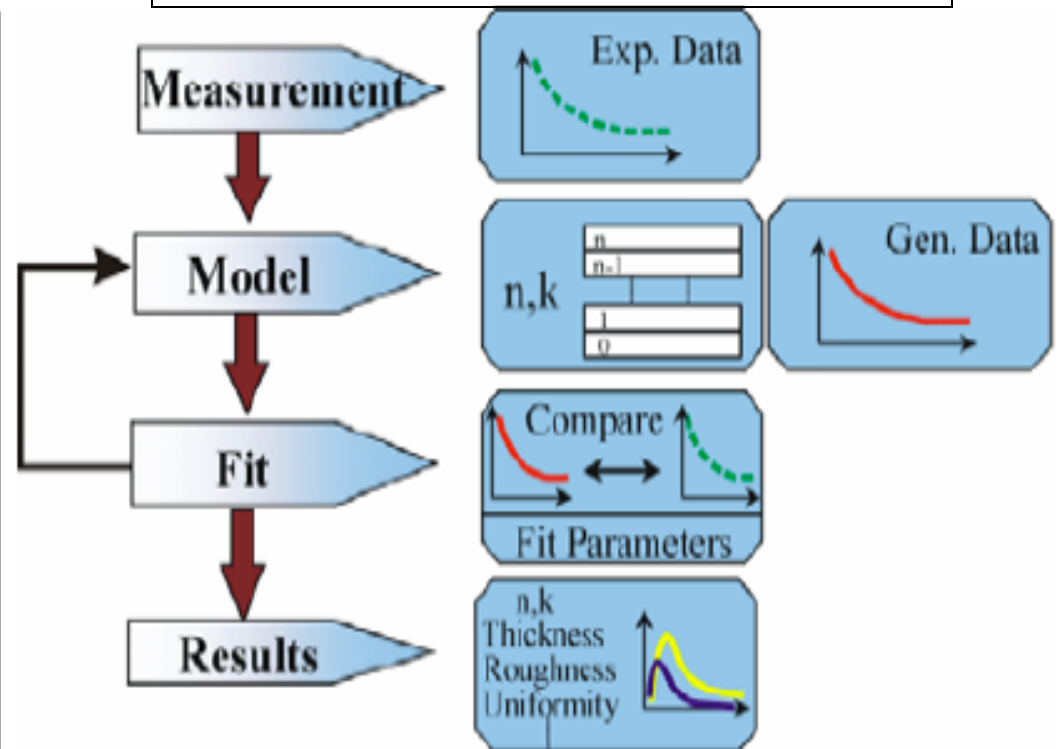


$$\rho = \frac{R_p}{R_s} = \tan(\psi)e^{i\Delta}$$

R_p, R_s are the complex Fresnel reflection coefficients

• Ellipsometry

- measures Δ and Ψ with 1-3 mm spatial resolution as a function of energy at several angles of incidence
- **Constants $(n, k, \epsilon_1, \epsilon_2)$**
- are derived –for layered samples- by fitting optical materials models (Cauchy, Urbach, Oscillator ..model)
- For a non-layered material optical constants can be derived directly without using a model – and then be compared to optical materials models
- The quality of fit is determined by calculating the mean square error (MSE) value.



Two independent models were used: 1) Cauchy-Urbach plus point by point extension {Kramers-Kronig checked}, 2) Gauss- or Lorentz Oscillators

1) **Cauchy's equation**

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^3} + \dots$$

is an empirical relationship between the refractive index n and the wavelength λ of a **transparent** material. $A, B, C \dots$ are coefficients determined by *fitting* to measured optical parameters. In a wavelength range where a material is slightly absorbing "Urbach extinction" is used to describe the extinction coefficient k .

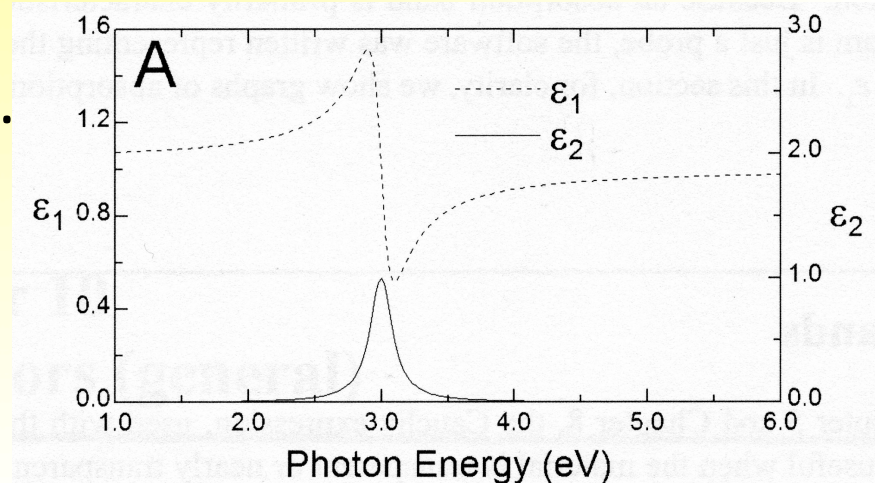
2) The **Urbach equation adds absorption**

$$k(\lambda) = A_k e^{B(E-E_k)}, \quad E = \frac{1240}{\lambda}, \quad \text{and} \quad E_k = \frac{1240}{\lambda_k}$$

3) **Kramers-Kronig consistency** of n and k (and hence ϵ_1, ϵ_2) is confirmed by checking that indeed

$$\epsilon_1(E) - 1 = \frac{2}{\pi} P \int_0^\infty \frac{E' \epsilon_2(E')}{E'^2 - E^2} dE', \quad \text{where } P \text{ is a constant}$$

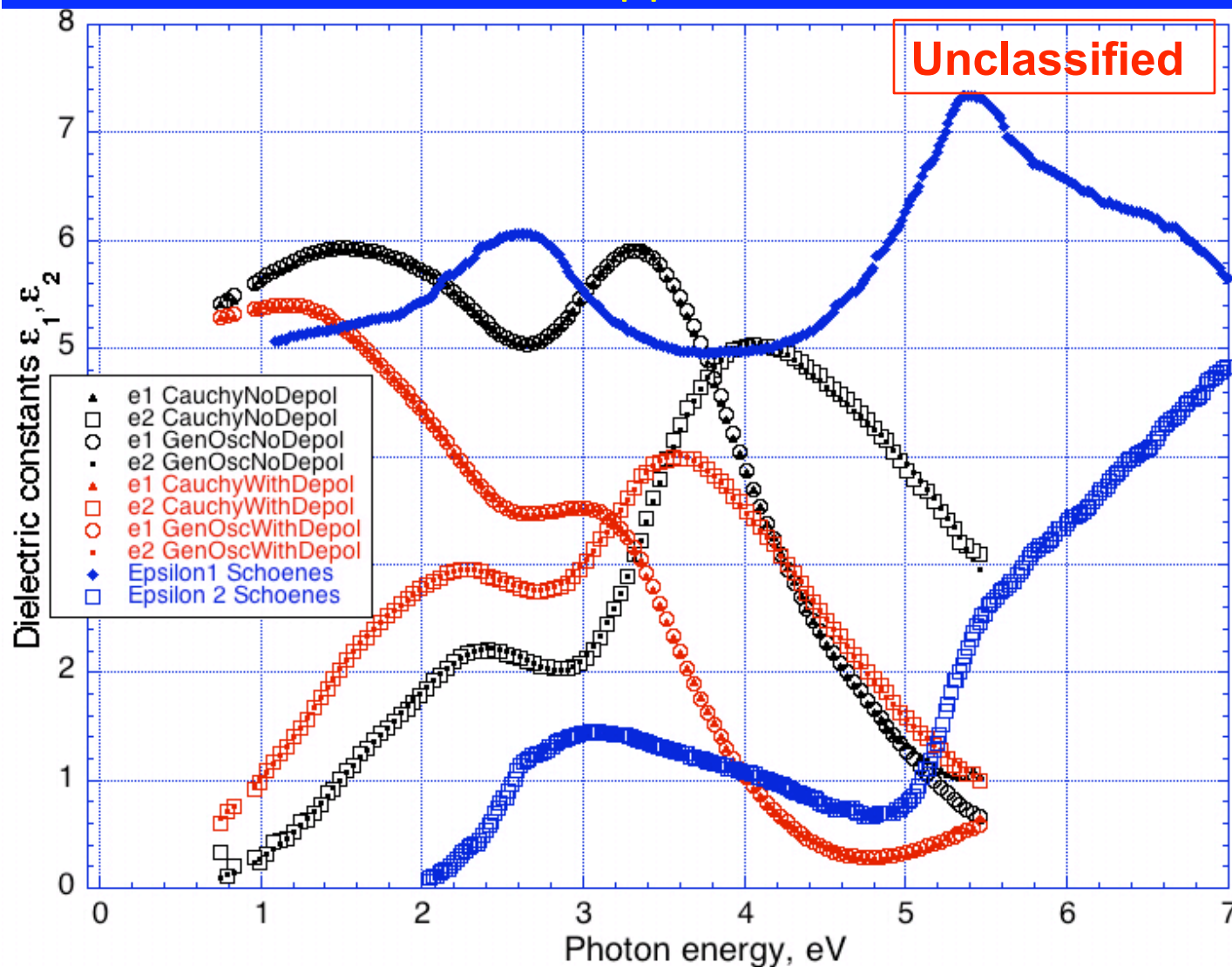
4) **Gauss-Lorentz and Tauc-Lorentz oscillators ..** model significant absorption in the spectral range of interest, due to either molecular vibrations or electronic absorption bands. A Lorentz oscillator, centered at 3 eV, is shown in figure A-> in the ϵ_1, ϵ_2 photon energy representation.



Ellipsometric data (Δ and Ψ) were taken under two different conditions

- Experimental condition 1: "isotropic"
 - Assumes the sample to be isotropic (as UO_2 with a cubic (fluorite) crystal structure should be)
- Experimental condition 2: "isotropic + depolarization"
 - Makes no assumption about the crystal structure
- If the results differ, it implies that the sample contains non-isotropic features

Ellipsometric data taken with and without depolarization produce substantially different dielectric constants, both different from Schoene's results. Our sample contains non-isotropic (i.e. non-cubic) features – which do NOT appear to influence Raman spectra

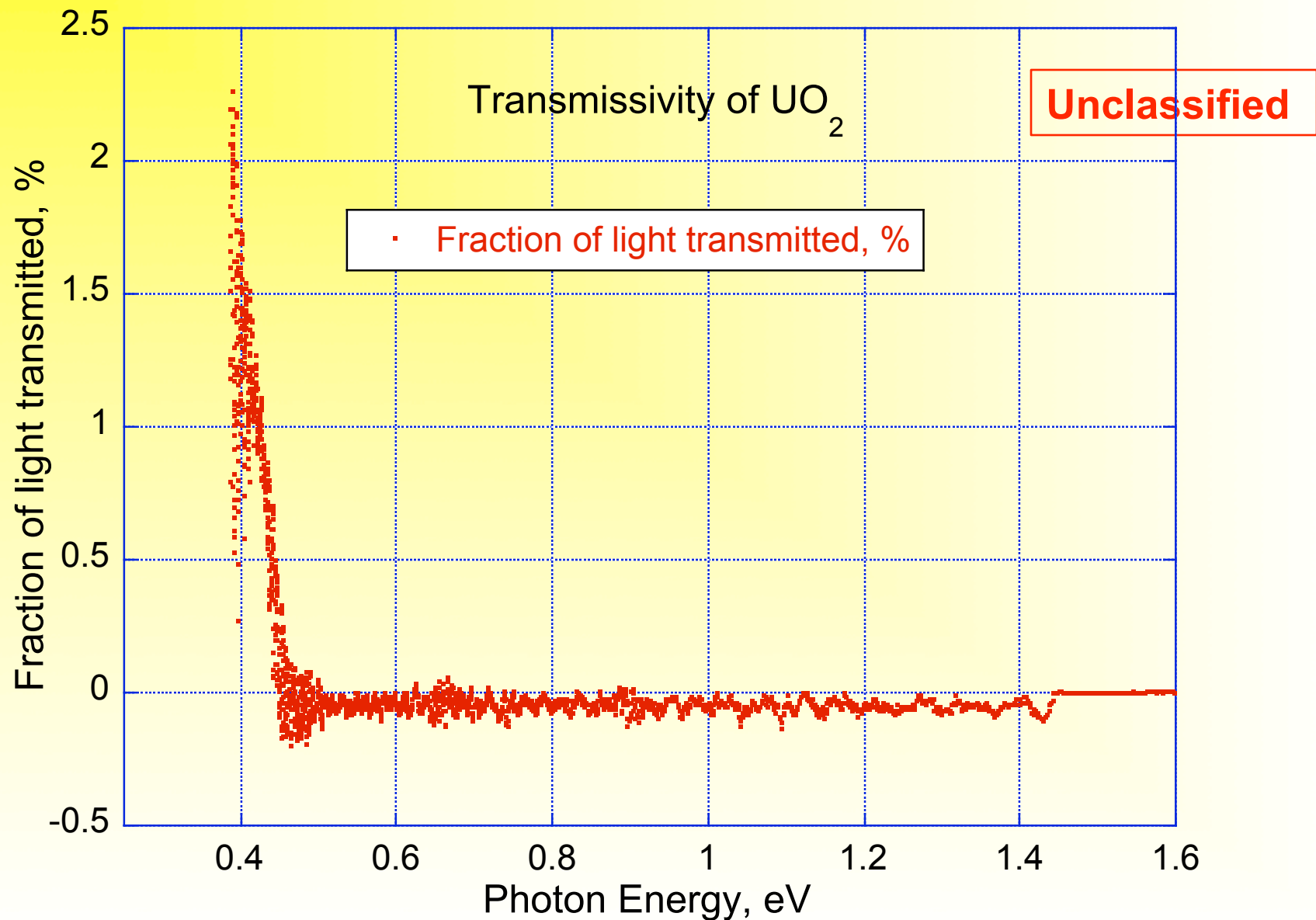


Black curves: ϵ_1 and ϵ_2 for experimental condition 1: “isotropic”. Fit to Cauchy or General oscillator models

Red curves: ϵ_1 and ϵ_2 for experimental condition 2: “isotropic +depolarization. Fit to a Cauchy or a General oscillator model

Blue curves: Schoene's ϵ_1 and ϵ_2 values. Zero values of ϵ_2 below 2 eV imply that the UO_2 is transparent there. Our sample is NOT transparent, see next viewgraph.

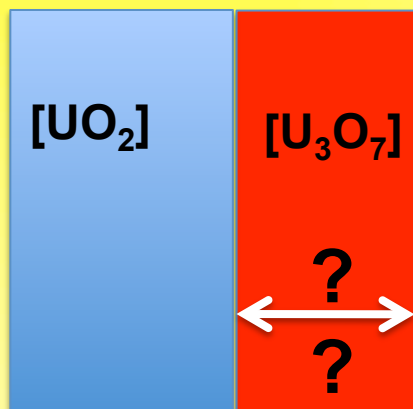
Transmissivity measurements with a HP spectrophotometer show that our UO sample is NOT transparent at energies above 0.5 eV



Did oxidation of UO_2 cause the difference between our ellipsometry results and Schoene's data?

1)

Unclassified



- Literature predicts by extrapolation from higher temperatures an U_3O_7 layer greater than 8 nm thick after exposure to air for 25 years at 300 K.

The Raman spectrum of UO_2 at 632 nm is not very surface-sensitive: it originates from an average depth of 84nm, while the ellipsometry signal at the highest energy (5.5eV) comes from an average depth of 2.6 nm

Both the incoming and the exiting light of wavelength λ is attenuated by the substrate

$d\text{Signal}_{\text{gen}}(x)$ = optical signal generated at depth x

$\alpha(\lambda)$ = absorption coefficient at wavelength $\lambda = 4\pi\kappa/\lambda$

$\sigma(\lambda)$ = Raman or scattering cross-section at wavelength λ

$d\text{Signal}_{\text{gen}}(x)_{\text{out}}$ = optical signal generated at depth and emerging from the surface

Unclassified

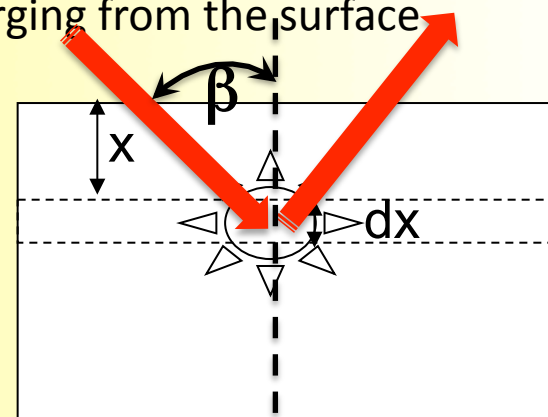
$$d\text{Signal}_{\text{gen}}(x) = I_0 \sigma(\lambda) e^{-\alpha(\lambda)x / \cos \beta}$$

$$d\text{Signal}_{\text{gen}}(x)_{\text{out}} = I_0 \sigma(\lambda) e^{-2\alpha(\lambda)x / \cos \beta}$$

$$\text{Signal}_{\text{out}} = \int_0^\infty I_0 \sigma(\lambda) e^{-2\alpha(\lambda)x / \cos \beta} dx = \frac{\cos \beta}{2\alpha(\lambda)}$$

$$d\text{Signal}_{\text{gen}}(x)_{\text{out,normalized}} = \frac{d\text{Signal}_{\text{gen}}(x)_{\text{out}}}{\text{Signal}_{\text{out}}} = \frac{2\alpha(\lambda) e^{-2\alpha(\lambda)x / \cos \beta}}{\cos \beta}$$

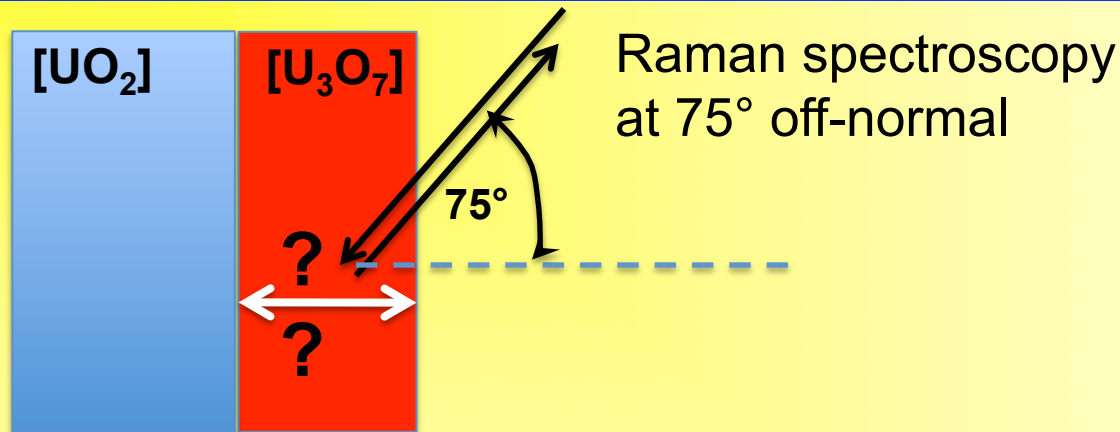
$$\text{Signal}_{\text{out}} \text{AverageDepth} = \langle x \rangle_{\text{SignalOutAverage}} = \int_0^\infty x \frac{2\alpha(\lambda) e^{-2\alpha(\lambda)x / \cos \beta}}{\cos \beta} dx$$



At $\lambda = 632$ nm(Raman), $\kappa = .3$, $\beta = 0$, $\alpha(\lambda) = 4\pi\kappa/\lambda$, $\langle x \rangle_{\text{SignalOutAverage}} = 83.82\text{nm}$

At $\lambda = 225$ nm(Ellipsometry), $\kappa_{\text{max}} = 1.2$, $\beta = 70^\circ$, $\alpha = 4\pi\kappa/\lambda$, $\langle x \rangle_{\text{SignalOutAverage}} = 2.55\text{nm}$

Raman spectroscopy at 75° off-normal incidence showed that the U_3O_7 oxide layer is much thinner than literature predicts.



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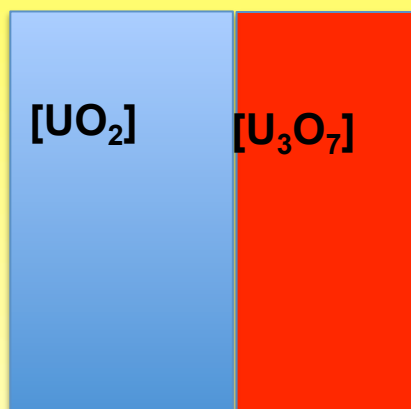
- Raman spectroscopy was done at 75° off-normal incidence using 632nm ($k=.3$) and 457nm ($k=.45$) laser light
- The measured optical absorption k ($k=.3$ @632nm, $k=.45$ @ 457nm) was used to calculate the average depth of the Raman signal
 - @ 632 nm 35% of the signal originates in the first 8nm
 - @ 457 nm 54% of the signal originates in the first 8nm
- Nevertheless: Raman spectra showed pure UO_{2+0} values
 - Hence: the U_3O_7 layer is much thinner than literature predicts
 - and our optical constants do correctly represent UO_2

Conclusion

Unclassified

Raman analysis of [111] UO_2 exposed 25 years to air shows only UO_2 lines. →
1) the oxidation rate of UO_2 to U_3O_7 is slower @ 300 K than listed in literature.
2) Ellipsometry's dielectric constants differ substantially from Schoenes's, and implying that this sample contains non-cubic features.

1)



- Literature predicts by extrapolation from higher temperatures an U_3O_7 layer greater than 8 nm thick after exposure to air for 25 years at 300 K.
- Raman analysis at 0° and 75° angle of incidence finds only UO_2
 - The extrapolation over-estimates U_3O_7 growth @ 300K
- Poulesquen, A., L. Desgranges, et al. (2007). "An improved model to evaluate the oxidation kinetics of uranium dioxide during dry storage." Journal of Nuclear Materials 362(2-3): 402-410.

2) Ellipsometric measurements of ε_1 and ε_2 (black and red) of UO_2 [111], show substantial disagreement with Schoenes' values (solid lines) calculated from near-normal reflectance. Schoenes, J. (1978). "Optical-Properties and Electronic-Structure of UO_2 ." Journal of Applied Physics 49(3): 1463-1465.

